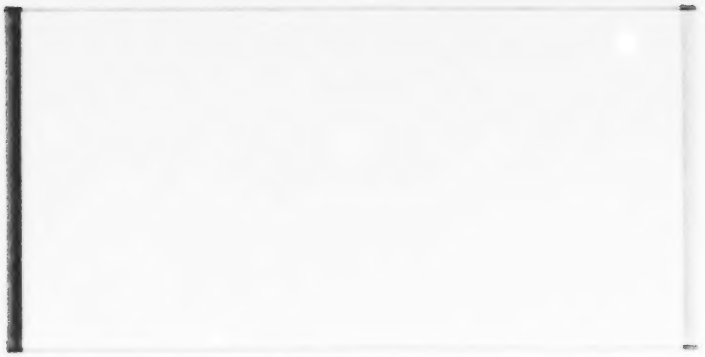
Ontario Hydro



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A PLANT FOR IMMOBILIZING LOW LEVEL LIQUID WASTE IN WATER EXTENDIBLE POLYMER

Report No 86-47-K

A. Husain
Engineer
Organic Research Section
Chemical Research Department

ABSTRACT

A description of a prototype plant for immobilizing low level decontamination wastes in water extendible polymer is presented. The plant can process aqueous wastes at the rate of 4 to 5 L/min. The equipment can be operated under a manual or semi-automatic mode. Experience gained in commissioning the equipment is documented. Present testing has been performed under the manual mode and using service water. Further evaluation is planned in the semi-automatic mode and using simulated wastes.

job	file	date	report no
740632-586-062	837.83	May 21, 1986	86-47-K

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EXECUTIVE SUMMARY

A PLANT FOR IMMOBILIZING LOW LEVEL LIQUID WASTE IN WATER EXTENDIBLE POLYMER

A. Husain
Engineer - Organic Research Section
Chemical Research Department

This report presents a description of a prototype plant for immobilizing low level aqueous wastes in water extendible polymer (WEP). The wastes arise from routine chemical and non-chemical decontaminations of radioactive equipment at Ontario Hydro nuclear stations. Waste solutions for which the 'decay, dilute and disperse' philosophy is not appropriate have to be immobilized before storage. Previous investigations using WEP polyester resin for immobilizing the decontamination wastes demonstrated that a satisfactory waste form with good leaching resistance is obtained. This immobilization technique will be the basis for solidifying low level wastes at Darlington.

The immobilization process involves the formation of an emulsion between the aqueous waste and the resin and its subsequent solidification by addition of a suitable catalyst/promoter combination. Waste concentrations as high as 700 g/kg product can be obtained with the liquid waste being sealed in the closed cell structure of the cured composite.

The emulsion is generated by metering the waste solution and polyester resin to a high speed mixing emulsifying chamber. The emulsion continuously discharges into a mechanical line blender wherein a metered catalyst (methyl-ethyl-ketone peroxide) stream is blended with it. The catalyzed emulsion is then collected into product containers. (Gel times are typically in the order of a few minutes; the product cures to a hard solid in a few hours.) Provisions have been made to flush the equipment after use with service water and/or solvent (methylene chloride). The plant can process aqueous wastes at the rate of 4 to 5 L/min.

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The equipment is wired up to permit operation under a manual or semi-automatic mode. In the latter mode, the resin, waste and catalyst pumps are simultaneously shutdown after a pre-determined length of time to fill the product container. The pumps are re-started in appropriate order following the replacement of the filled container with an empty one.

Difficulties encountered in commissioning the WEP equipment are described in detail. Present testing has been performed under the manual mode and using service water. Further evaluation is planned in the semi-automatic mode and using simulated wastes. It is expected that a compact version of the equipment would subsequently be installed at Darlington NGS. Similar equipment may also be mounted on a mobile skid for use at any plant.

Acknowledgement

The contributions of Mr. A.S. Williamson, Mr. L.S. Krochmalnek, Dr. S.H. Hawthorne, Mr. M.K.G. Stelter, Mr. R.K. Cleary and Mr. B.D. Aucoin are gratefully acknowledged.

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To Dr. D. Mills
Director of Research

A PLANT FOR IMMOBILIZING LOW LEVEL LIQUID WASTE IN WATER EXTENDIBLE POLYMER

1.0 INTRODUCTION AND BACKGROUND

Aqueous low level radioactive wastes at the nuclear stations arise from routine chemical and non-chemical decontaminations of equipment. Solutions for which the 'decay, dilute and disperse' philosophy is not appropriate have to be immobilized before they can be stored at BNPDS. Previous investigations/1-3/ using water extendible polyester (WEP) as an immobilization agent have demonstrated that a satisfactory waste form with good leaching resistance is obtained. This immobilization technique will be the basis for solidifying low level aqueous wastes at Darlington NGS. The solid waste form would then be transported to BNPDS for storage and possibly volume reduction by incineration.

The immobilization process involves the formation of an emulsion between the aqueous waste and organic polymer and subsequent solidification of the emulsion by addition of a suitable catalyst/promoter combination. Waste concentrations as high as 700 g/kg product can be obtained with the liquid waste being sealed in the closed cell structure of the cured composite.

Krochmalnek/4/ has described in detail the design considerations for a WEP system to immobilize low level radioactive waste at Darlington. This has formed the basis for the procurement, assembly and operation of a full scale prototype aqueous waste solidification system at Research Division. The system is semi-automated and is operated from a local control panel. It may alternately be operated in a manual mode.

This report presents an account of the WEP system and its commissioning. At present, the system has undergone commissioning trials in the manual mode using inactive service water. Trials in the automatic mode will be undertaken soon and reported separately along with immobilization experience with simulated inactive decontamination wastes.

86-47

2.0 PROCESS FLOW SHEET

The flow sheet for the WEP system is shown in Figure 1. Waste solution from tank TK2 conditioned to pH 7-8 and the WEP resin (Ashland Chemical Co, Aropol WEP 661-P) from the resin drum are metered at 0.08 to 0.27 m^3/h to a mixing-emulsifying chamber to produce a water-in-resin emulsion containing $\geq$50 wt % waste. The methyl-ethyl-ketone peroxide catalyst (Lucidol Lupersol DSW-9) is metered at 0.001 to 0.01 m^3/h (0.5 to 2 wt % resin) and blended with the emulsion in the mechanical line blender. The catalyzed emulsion continuously discharges from the line blender into a product container. Provisions have been made (1) to permit liquid waste to be pumped from a drum into tank TK2 and subsequent mixing and pH adjustment of its contents and (2) for service water/solvent flush of the emulsifying chamber and line blender at the end of an immobilization.

Photographs of the emulsifying chamber, line blender and the WEP system are shown in Figures 2 to 4.

A list of the main process equipment, flow calibration data and detailed manual operating instructions are given in the Appendices.

3.0 IMMOBILIZATION SYSTEM CONTROL

The control strategy for operating the immobilization system has been described in detail elsewhere/4/. The main control system is depicted in Figure 5. Briefly, the 4 to 20 mA signals from the three flowmeters are added in accordance with appropriate scaling factors to obtain the composite 4 to 20 mA signal corresponding to the total flowrate entering the product container. When this signal converted to a voltage pulse and accumulated over time corresponds to the volume of the product container, control action is taken to shut off the metering pumps. Following replacement of the filled container, operations are resumed by manually activating the pumps.

4.0 PROBLEMS ENCOUNTERED DURING COMMISSIONING AND THEIR RESOLUTION

Several problems were encountered during the commissioning of the immobilization system. Initial difficulties were due to inappropriate selection of some of the process equipment. The problems and their resolution are itemized below.

1. A diaphragm metering pump was originally selected for the catalyst service. The pulsatile flow delivered by the pump caused improper catalyst distribution in the emulsion

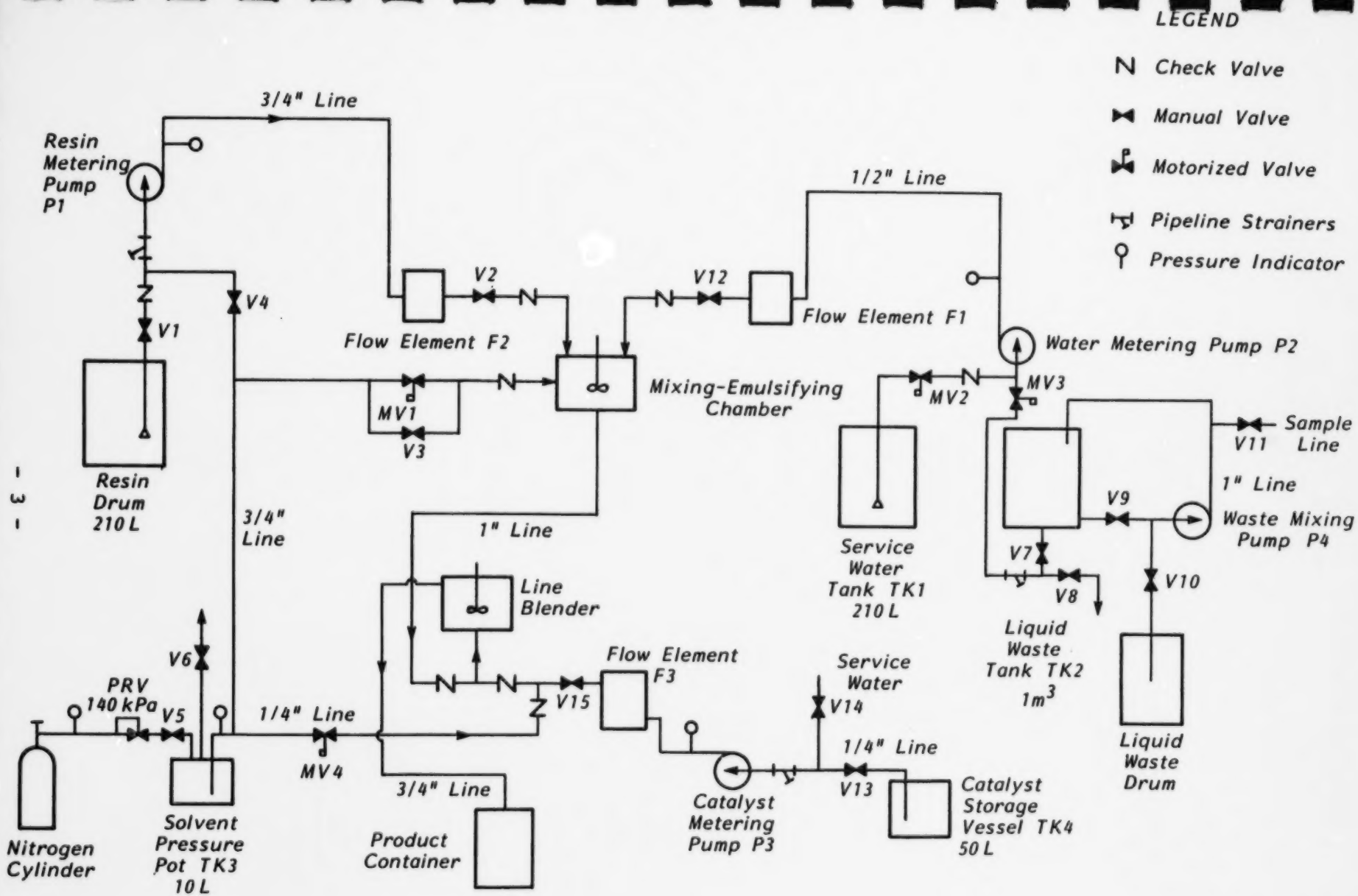
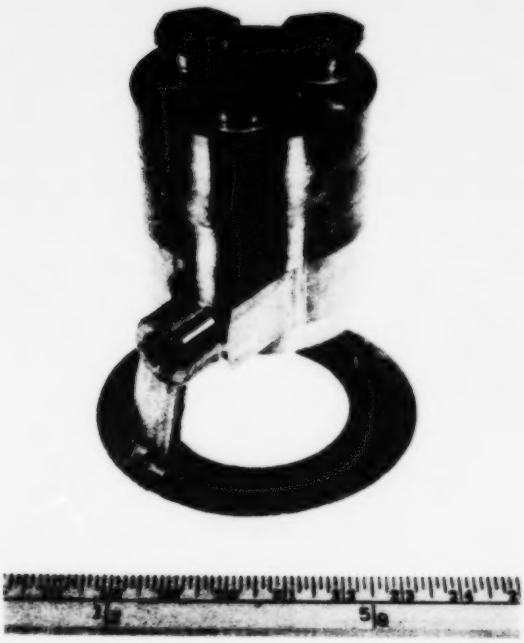


FIGURE 1

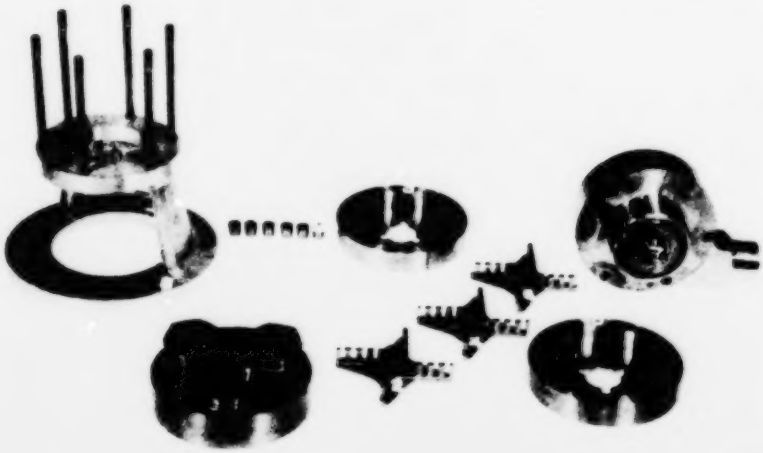
RESEARCH DIVISION DEMONSTRATION PLANT
DECONTAMINATION SOLUTIONS
SOLIDIFICATION SYSTEM FLOW DIAGRAM

86-47



(a)

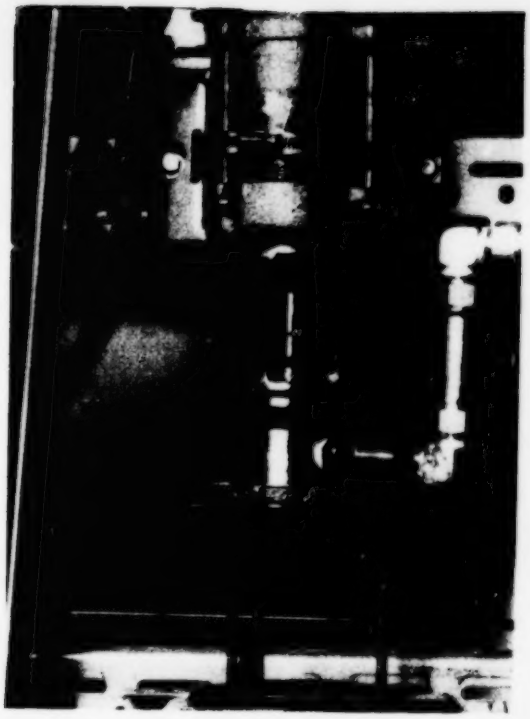
(b)



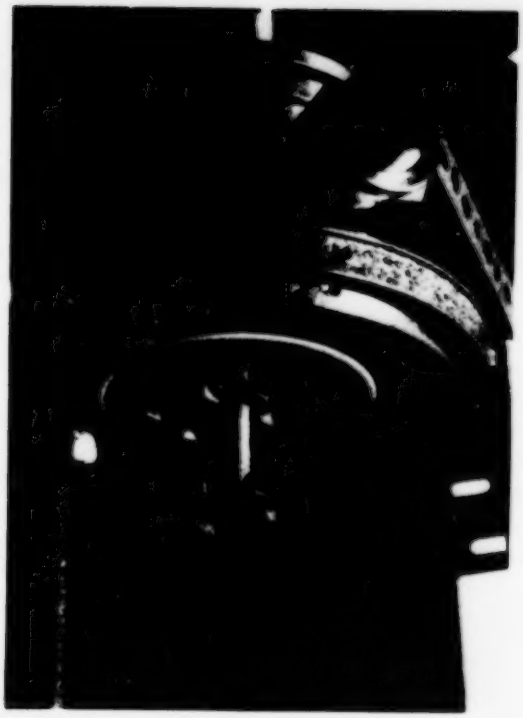
(c)

FIGURE 2

THE MIXING EMULSIFYING CHAMBER
(a) OVERALL VIEW OF THE EMULSIFYING CHAMBER
(b) INTERNAL VIEW OF THE EMULSIFYING CHAMBER SHOWING THE IMPELLERS
(c) DISASSEMBLED COMPONENTS OF THE EMULSIFYING CHAMBER



(a)



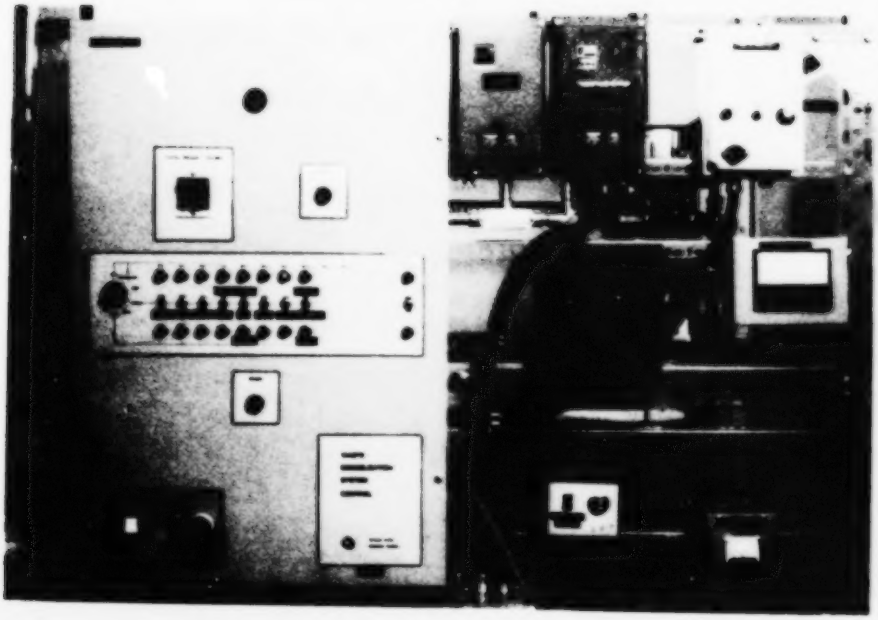
(b)

(c)

FIGURE 3

THE LINE BLENDER
(a) OVERALL VIEW OF THE BLENDER
(b) INTERNAL VIEW OF THE BLENDER SHOWING THE IMPELLERS
(c) IN OPERATION SHOWING THE EMULSION POURING OUT FROM IT

(a)



(b)

FIGURE 4

THE WEP SOLIDIFICATION DEMONSTRATION PLANT
(a) OVERALL VIEW (b) CONTROL PANEL, FLOW CONTROLLERS AND OTHER CONTROL EQUIPMENT

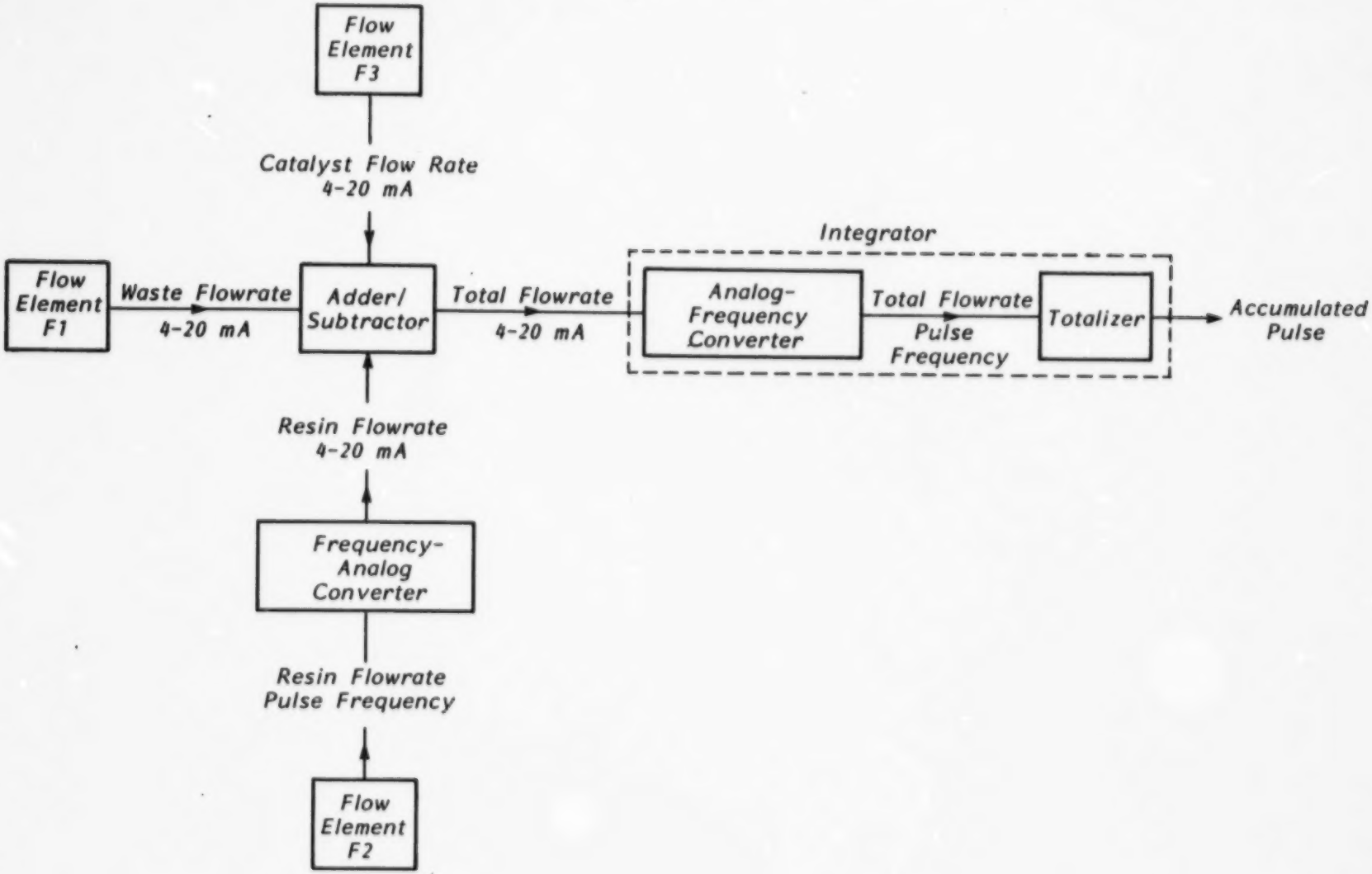


FIGURE 5

BLOCK DIAGRAM OF THE MAIN CONTROL SYSTEM

resulting in non-uniform product curing. The pump and its associated controller were subsequently replaced with a pulse-free metering pump (a Micro pump Model) which is operated using a 0 to 24 V DC power supply.

2. Since variations in viscosity between resin batches was not anticipated, the flowmeter originally procured for metering the resin was of the meter tube and float type. Unreliable metering using this flowmeter led to its replacement with a viscosity independent Brooks oval gear flowmeter. Unlike the previous flowmeter which generated a 4 to 20 mA output signal, the Brooks instrument generates a voltage pulse. To maintain compatibility with the other control equipment, the pulse is, therefore, fed into a frequency to analog converter (as shown in Figure 5) with an output of 4 to 20 mA.

3. A motionless Greey Lightnin mixer was originally selected for blending the catalyst into the emulsion. Due to insufficient mixing, the catalyzed emulsion repeatedly failed to gel. No significant improvement occurred with two of the mixers in series. Replacement of the motionless mixer with a mechanical (operating at 1750 rpm) line blender in combination with catalyst metering using the new Micropump yields a well-mixed emulsion which gels and cures reproducibly.

4. Strainers were installed at all pump inlets to avoid a reoccurrence of equipment downtime due to lodging of debris within pump housings and to protect the flowmeters. The strainer at the resin pump inlet was found to be the most susceptible to clogging due to partial polymerization of the resin during extended shutdowns.

5. The 1-1/2" line size originally connected to the outlet port of the emulsion head was downsized since the connections on the line blender are of 1/2" size. Downsizing to 1/2" resulted in a reduction of the waste flowrate at previously calibrated controller settings although no adverse effect occurred on the resin flowrate. The problem was particularly acute with the emulsion head operating. Improvements were noted with the use of 3/4" or 1" line size. During this assessment, the motor coupled to the emulsion head tripped occasionally and seals in the emulsion head developed a leak.

Subsequent dismantling of the emulsion head indicated considerable deterioration of the metal seals and bearing. In addition, rusty patches were observed on the impeller surfaces and some of the impeller mounting screws had cracked. Replacement of the deteriorated parts (seals should

preferably be made of viton) restored the emulsion head to its original service condition.

The seal failure is believed to have resulted from gradual deterioration during service particularly from exposure to the methylene chloride solvent. The increased back pressure due to operation with a 1/2" line size may have aggravated the seal condition but is unlikely to have been directly responsible for its failure. Nevertheless, to avoid a re-occurrence of this problem, a 1" line size was chosen, reduction below which is not considered advisable.

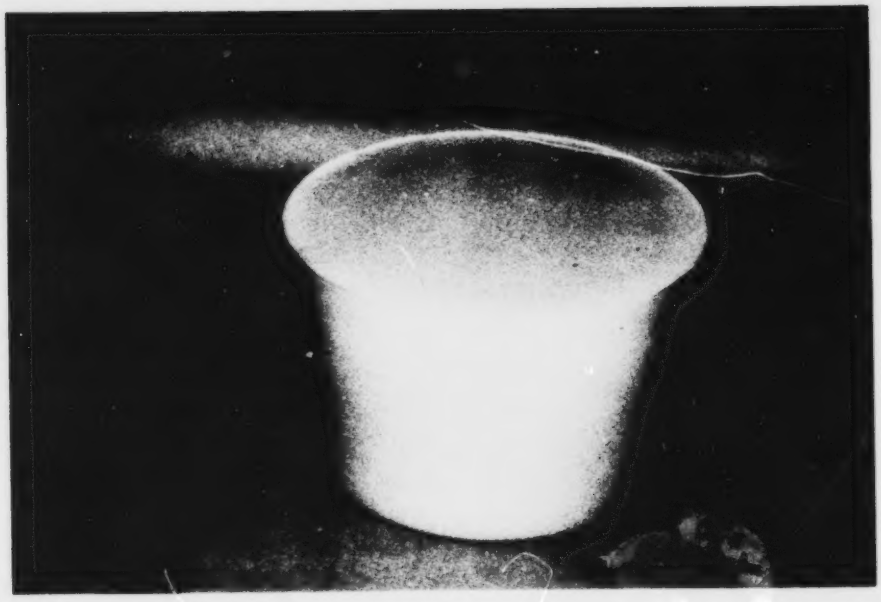
6. An attempt to solvent flush the line blender at the end of an immobilization resulted in motor overload due to a 15 to 30 s delay in admitting solvent to dilute the catalyzed emulsion in the blender and associated tubing. It is imperative for the safe operation of the blender that the catalyzed emulsion be completely displaced prior to admitting solvent.

7. Binding of the blender shaft, although not excessive, was experienced occasionally following an overnight shutdown. As this probably occurred due to gelling of residual (after flushing) emulsion at the seal location, a short section of the product container filling line at the blender outlet was raised above the level of the blender. During flushing, the resulting hydrostatic head ensures solvent access in the seal region; also, closure of the motorized valve MV4 following a solvent flush permits an extended soak of the blender internals.

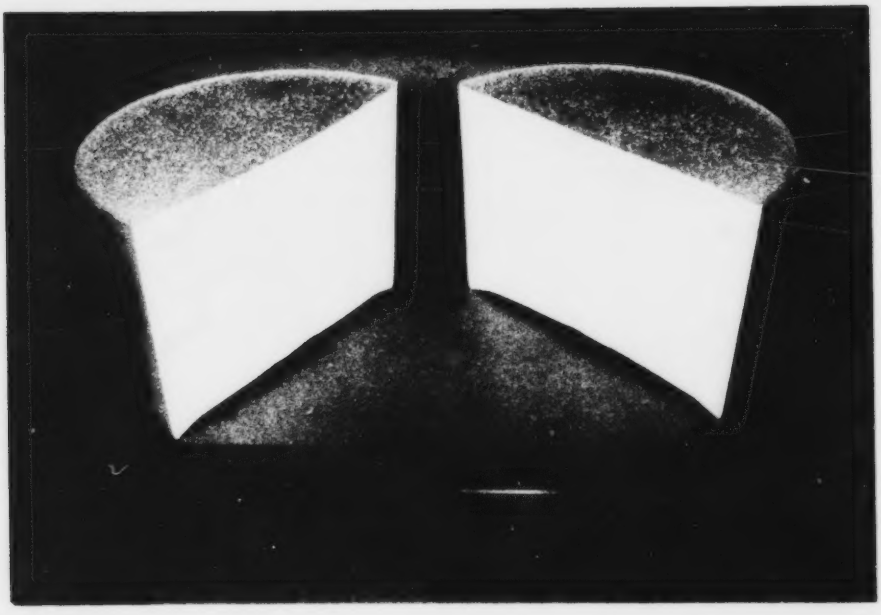
5.0 WEP SYSTEM - IMMOBILIZATION EXPERIENCE

Several immobilization trials were conducted. Generally a 1:1 resin-water emulsion was produced with the catalyst content varying between 1/2 to 1 wt % of the resin. The resin and water flowrates were varied between 1 to 4 L/min. In all cases, the emulsion gelled within a few minutes; an overnight cure yielded a satisfactory solid waste form. To minimize resin usage the largest product container filled was restricted to about 15 L. Figure 6 shows a typical waste form produced and its cross-section.

The line blender is capable of handling a flow rate of up to 6 L/min of materials with a viscosity of up to 1000 cp. At 8 L/min emulsion (resin and water flow rate each 4 L/min) flow rate, the handling capacity of the blender is exceeded. However, sufficient residence time is still available to permit a homogeneous distribution of the catalyst in the emulsion as judged by the uniform product cure. Increasing the emulsion



(a)



(b)

FIGURE 6

SOLIDIFIED WASTE FORM PRODUCED BY THE
WEP DEMONSTRATION PLANT
(a) OVERALL VIEW
(b) CROSS-SECTIONAL VIEW

flowrate much above 8 L/min may be limited by insufficient catalyst blending. Further, a water:resin ratio greater than 1.5 is not recommended since the emulsion viscosity increases dramatically with water content.

Preliminary estimates of flush volumes were obtained as follows: the blender was initially flushed with water at 0.2 L/min until the effluent was clear. This was followed by solvent flush at a flow rate of 0.1 L/min (solvent pot pressurized to 3 psi). The total effluent collected was 1.5 L consisting of 1 L water and 1/2 L solvent. In the next stage, the emulsion head was successively flushed with water at 1 L/min and solvent at 0.5 L/min (solvent pot pressurized to 5 psi) generating an additional 4 L effluent consisting of 2 L each of water and solvent. It should be possible with additional experimentation to significantly reduce the total flush volumes generated in the two stages.

The flushing sequence described above while repetitious in-so-far as the blender is concerned ensures that the catalyzed emulsion is displaced from the blender expeditiously. The delay in the opening of the motorized valve in the solvent line led to thickening of the emulsion in the blender with consequent motor overload when this sequence was not practiced.

6.0 CONCLUSIONS AND RECOMMENDATIONS

The WEP immobilization system now performs satisfactorily under manual operation. Specific recommendations for further work are:

1. implementation of the automatic control strategy,

2. determination of optimum start-up and flushing procedures so that secondary waste generation is minimized,

3. immobilization of simulated decontamination wastes to ascertain optimum catalyst requirements for each waste type, and

4. compaction of layout and mounting of the equipment on a mobile skid.

In the automatic mode, as currently envisioned, the WEP system would be operated semi-continuously. This intermittent operation is likely to cause considerable wear and tear on the equipment, particularly the flowmeters, because unlike in a manual mode, flows are initiated with the controllers preset to their desired settings thus exposing the process equipment to sudden flowrate changes. While additional equipment can be installed to ramp the flows, a simpler alternative is to operate the system continuously with two product filling stations. With suitable valving provisions, one container could be filled while the other filled one is being replaced with an empty one.

Incorporation of the secondary waste generated in the start-up and finishing stages with the emulsion in the product container is desirable. In fact Hawthorne/3/ observed no significant deterioration in appearance of products containing up to 30 g/kg methylene chloride. However, the concentration of solvent in the flushing waste is expected to be considerably higher than the above limit. Rather than imperil the adequate curing of a large batch of product, the secondary waste, small as it is relative to the total volume of primary waste solidified, should preferably be processed separately.

Lastly, the layout of the equipment should be revised to effect a significant reduction in floor space occupied. Appropriate steps should also be taken to enable the processing of active wastes and mounting of the equipment on a mobile skid suitable for transportation between nuclear stations.

7.0 ACKNOWLEDGEMENT

The contributions of Mr. A.S. Williamson to the conceptual design, Mr. L.S. Krochmalnek and Dr. S.H. Hawthorne to the initial engineering, Mr. M.K.G. Stelter to the automation, and Mr. R.K. Cleary and Mr. B.D. Aucoin in assembling and operating the WEP plant are gratefully acknowledged.

Approved:

O.A. Kupcis
Manager
Chemical Research Department

Submitted:

A. Husain
Engineer
Organic Research Section

Reviewed:

R.W. Glass
Supervising Chemist
Organic Research Section

AH:djb

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2. Williamson, A.S., "Solidification of Aqueous Decontamination Wastes With Water Extendible Polymers", Ontario Hydro Research Division Report No 81-57-H (1981).

3. Hawthorne, S.H., "Solidification of Aqueous Decontamination Wastes With Water Extendible Polymers - Darlington NGS", Ontario Hydro Research Division Report No C82-17-H (1982).

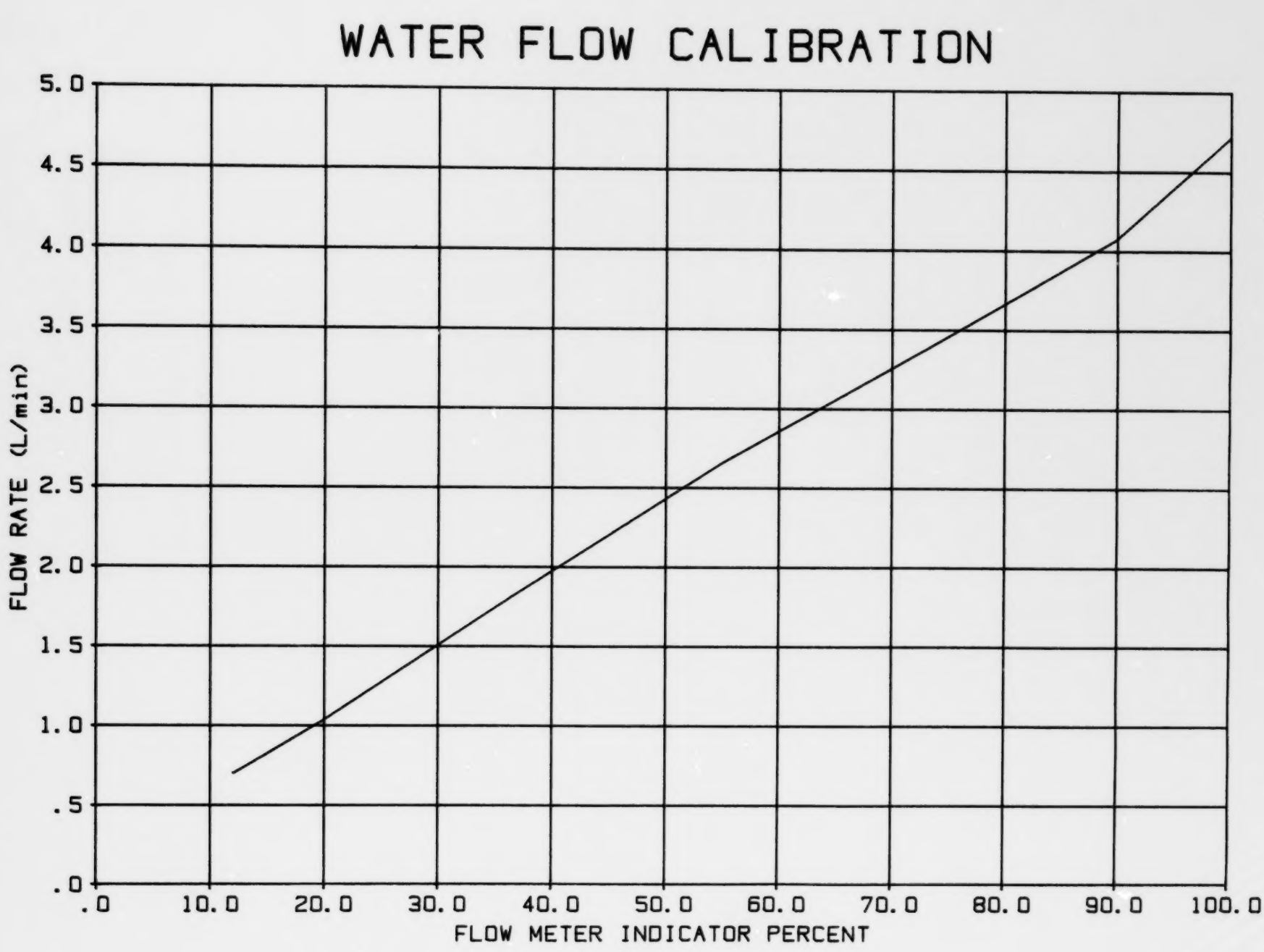
4. Krochmalnek, L.S., "Darlington NGS 'A' Decontamination Solutions Collection and Treatment", Revised Draft PDD-79750 (1983).

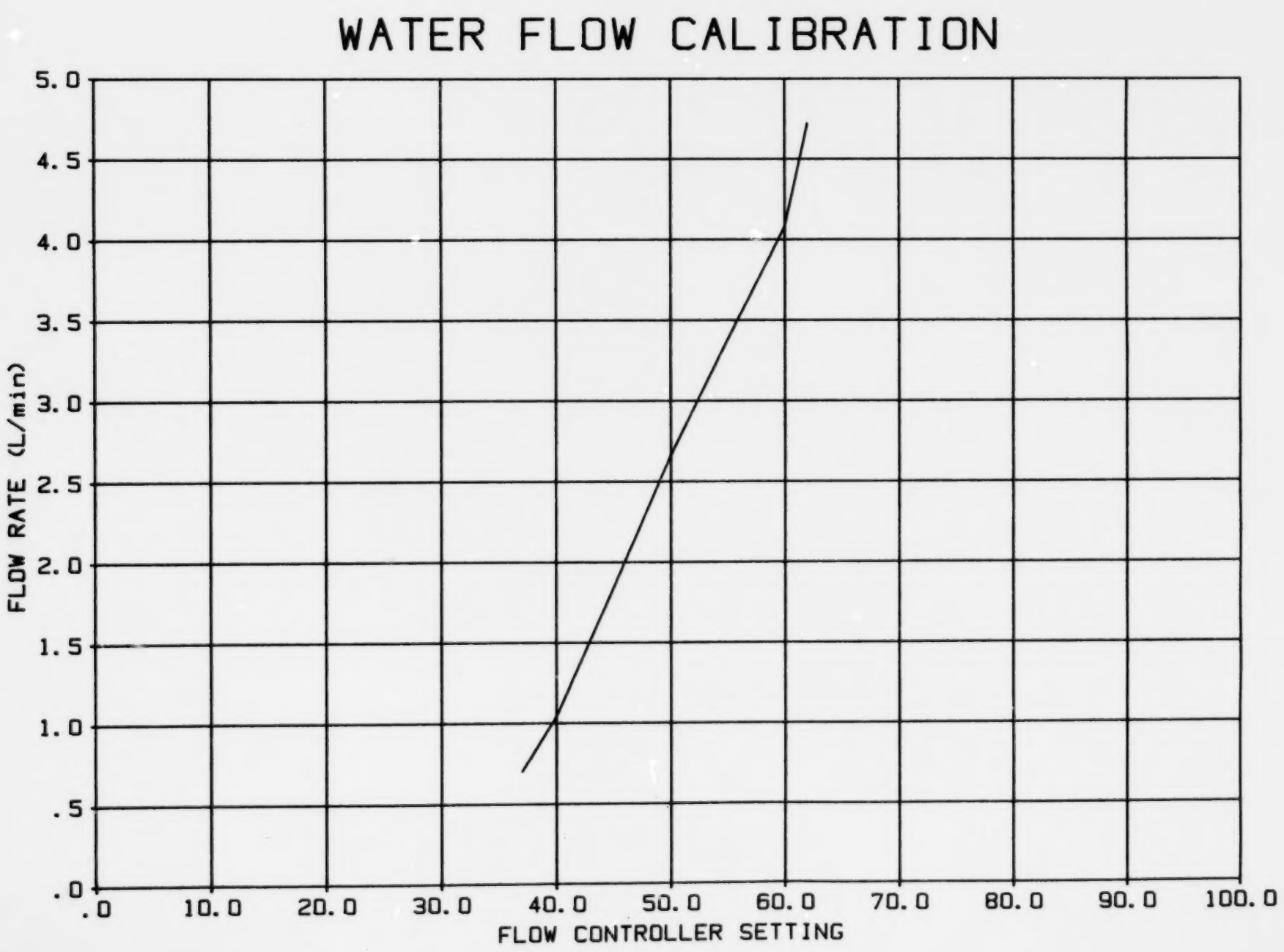
APPENDIX 1

CALIBRATION OF RESIN, WATER AND CATALYST FLOWS

Calibration curves for the three metering pumps are shown overleaf. While the meter reading (%) versus flowrate curves were reproducible, the controller settings versus flowrate curves (resin and waste) were less reliable and are recommended as an operational aid only. The calibration curves are essentially linear over the entire range of flowrates. As hoped for, the resin pump calibration was independent of the resin viscosity.

Response of the pumps to step changes in controller settings was virtually instantaneous for the resin and catalyst streams. The response was more gradual in the case of the waste pump. Note that the 100% flowmeter reading for the resin and water streams correspond in each case to the maximum design flow of 4.5 L/min although the pumps are capable of delivering larger throughputs. However, the 100% indication for the catalyst flow corresponds to about 12 L/h rather than the maximum design flow of 10 L/h. This may necessitate a re-adjustment of the catalyst flow scaling factor in the Adder/Subtracter. Ignoring this discrepancy, however, will not lead to any significant error in the totalizer output. As with the other pumps, the catalyst pump is capable of delivering considerably above the maximum design flow.


WATER FLOW CALIBRATION
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
.0
FLOW RATE (L/min)
.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
FLOW METER INDICATOR PERCENT


WATER FLOW CALIBRATION
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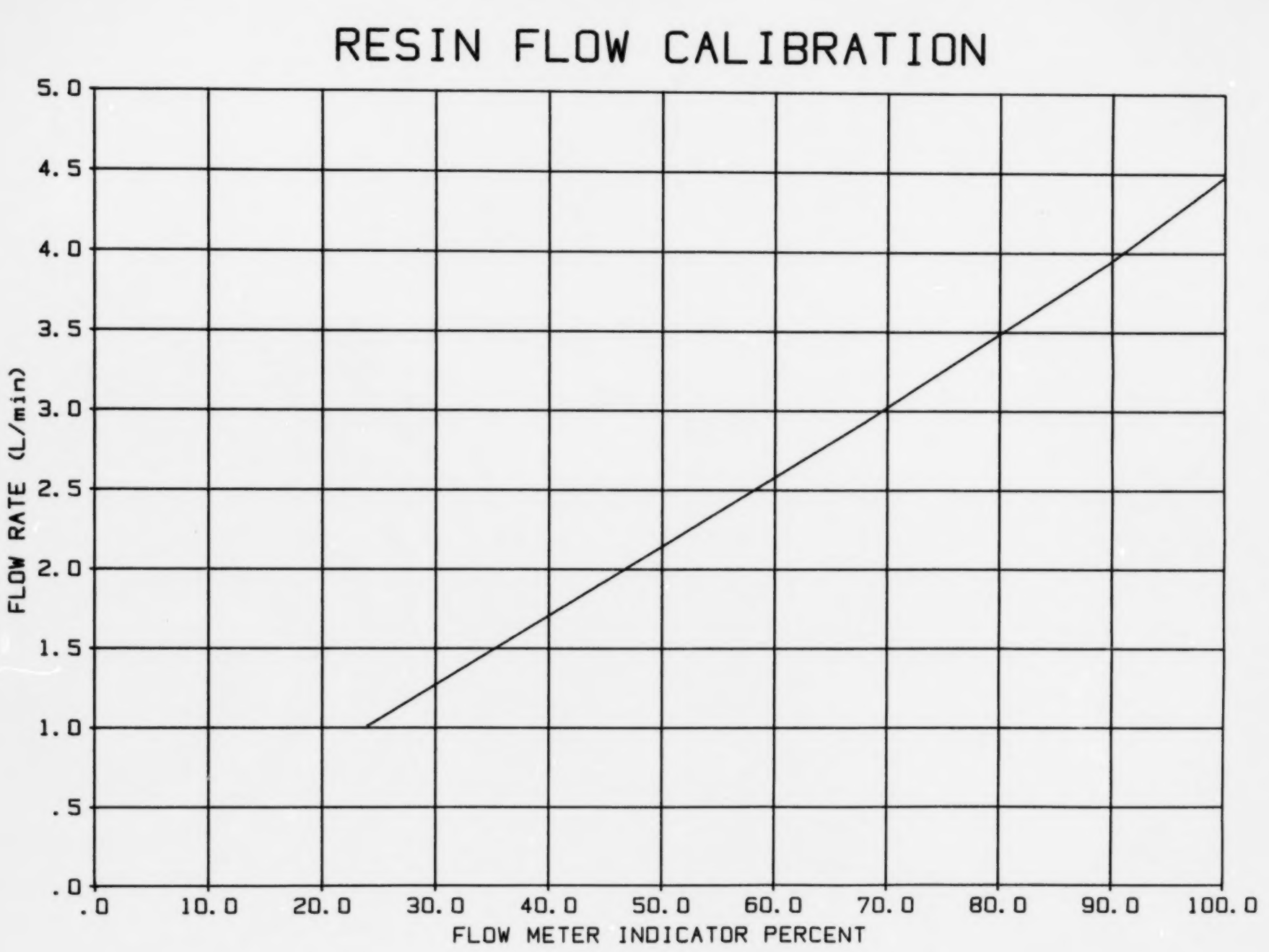
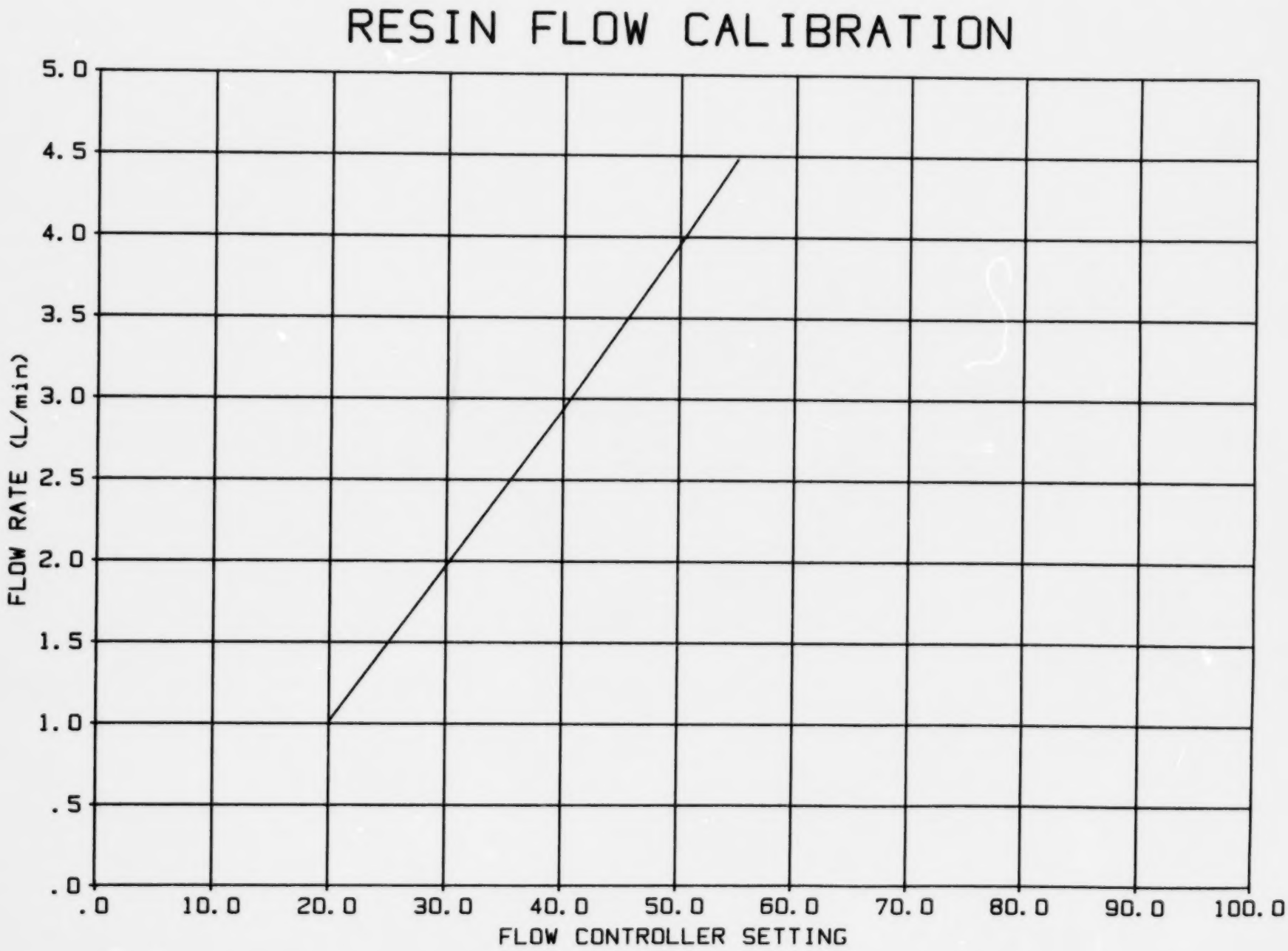
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
.0
FLOW RATE (L/min)
.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
FLOW CONTROLLER SETTING


RESIN FLOW CALIBRATION
FLOW RATE (L/min)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
.0
.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
FLOW METER INDICATOR PERCENT


RESIN FLOW CALIBRATION
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
.0
FLOW RATE (L/min)
.0
10.0
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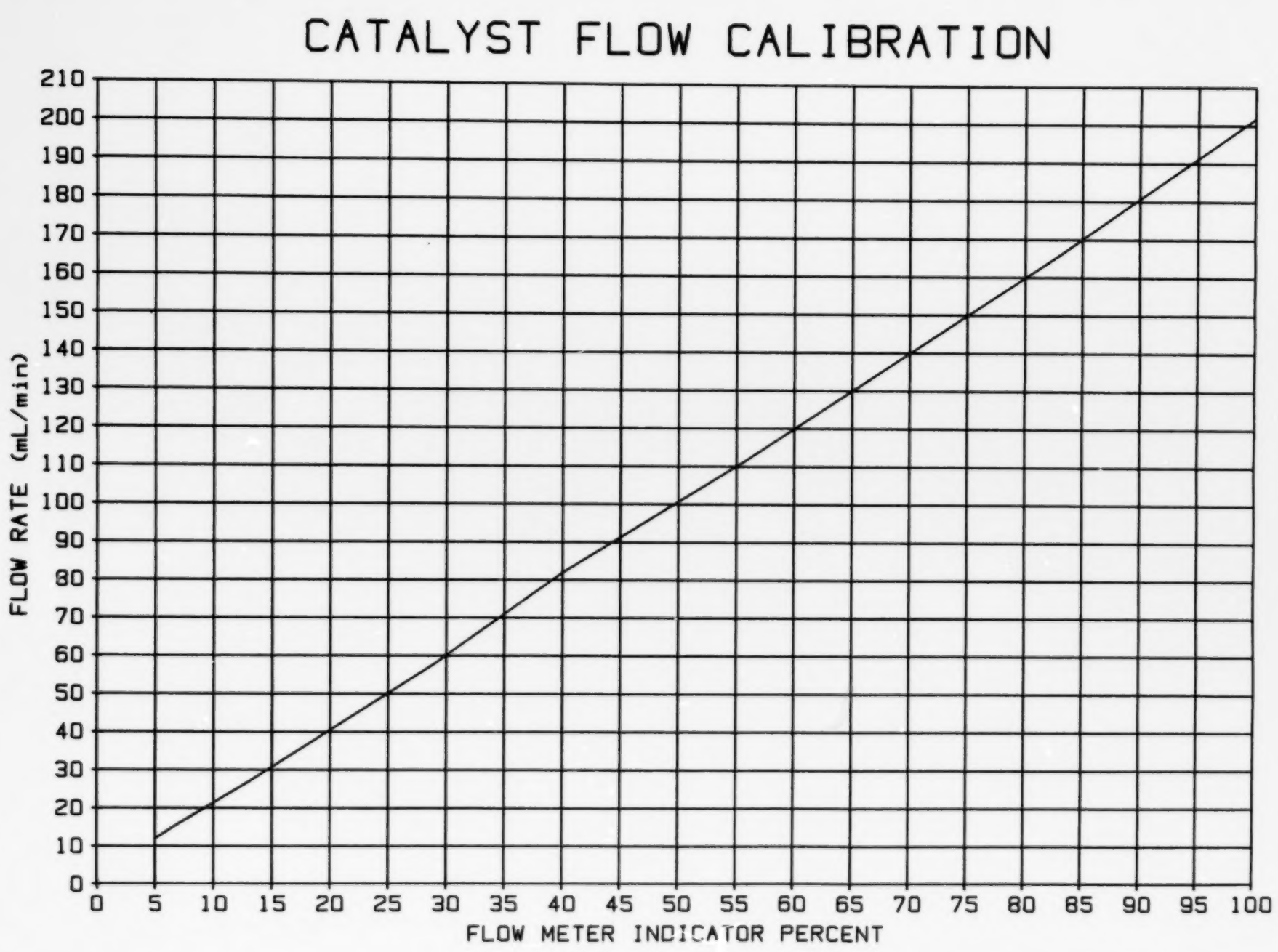
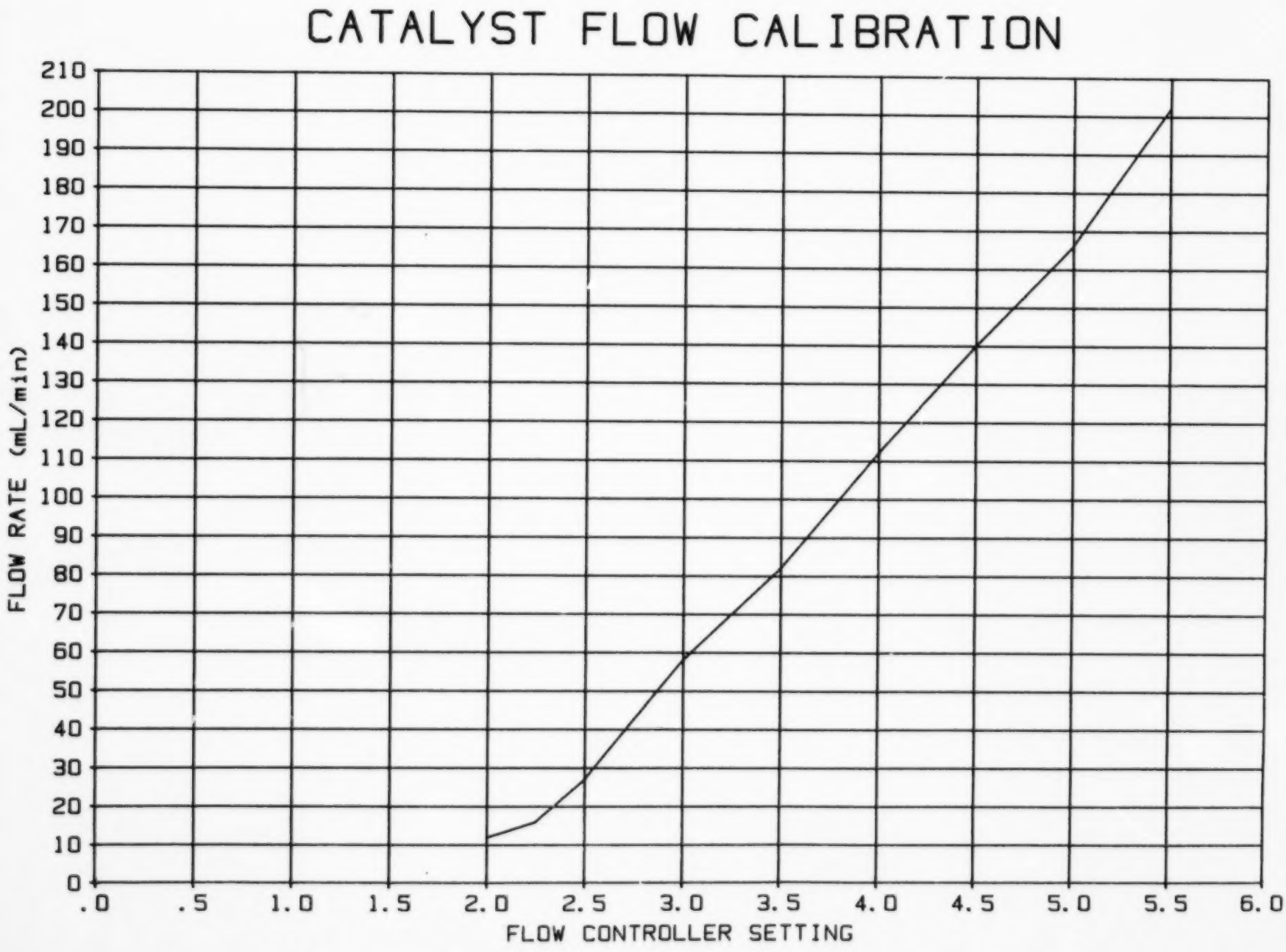
70.0
80.0
90.0
100.0
FLOW CONTROLLER SETTING


CATALYST FLOW CALIBRATION
FLOW RATE (mL/min)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
FLOW METER INDICATOR PERCENT


CATALYST FLOW CALIBRATION
FLOW RATE (mL/min)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
.0
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
FLOW CONTROLLER SETTING

APPENDIX 2

SPECIFICATIONS OF MAIN PROCESS EQUIPMENT

Equipment	Specifications
Pumps	
P1	Resin Metering Pump (ECO Gearchem Pump Model No G4ACCZTR) - self priming, SS316, gear pump, pump coupled to a variable speed drive 230 V AC motor (Underwriters Laboratories Model No M7003A), motor controlled by FHP ParaJust AC Motor Speed Control.
P2	Waste Metering Pump (ECO Gearchem Pump Model No G4ATTZTR) - self priming, SS316, gear pump, pump coupled to a variable speed drive 90 V DC motor (Indiana General Motor Products Model No 46304351543-0A), motor controlled by Doerr Electric's STEDI-DRIVE.
P3	Catalyst Metering Pump (Micropump Model 185-306) - self priming, SS316, magnetic gear pump, integral pump-motor assembly, variable speed drive 0-24 V DC motor controlled by a manual power supply/speed controller.
P4	Waste Mixing pump (ECO Gearchem Pump Model No G6ATTZTR).
Flow Elements	
F1	Waste Flowmeter (Fischer & Porter Model No 10A5004BABBX3F) - SS316, meter tube and float type.
F2	Resin Flowmeter (Brooks Model No 9417B3C1V2G)-SS316, oval gear meter.
F3	Catalyst Flowmeter (Fischer & Porter Mini-Mag-X Model No 10D1475CBBC11B) - SS316, magnetic flow meter.
Mixing Emulsifying Chamber	SS316 mixing head (Barlo Inc. Model No 567-110), head coupled to 2 HP, 3450 rpm, 220 V 3 phase motor.
Line Blender	SS316, direct drive mechanical line blender (Greey Lightnin Model No .025-LB-.05), 1750 rpm, 120 V single phase motor.

APPENDIX 3

WEP IMMOBILIZATION SYSTEM - MANUAL OPERATION

Instructions for the start-up and operation of the WEP system are described here. Shutdown procedures are still being revised and will be detailed later.

Start-up Phase

1. Make sure that all switches on control cabinet and settings on flow controllers (resin, waste and catalyst) are in the OFF position, and all valves are closed.

2. Switch on ventilation system.

3. Turn on main power and all switches on load centre (situated directly below main power switch box).

4. Fill solvent pot with methylene chloride. Open valve V5 in the solvent pot pressurizing line and pressurize pot to 3-5 psi.

5. Turn power on at control cabinet (all red lights on). Set black dial to manual mode. Switch on (lights turn green) resin pump P1, waste pump P2, catalyst pump P3 and open motorized valve MV3.

6. Examine and clean resin strainer if necessary (the other strainers do not require frequent examination).

7. Open valves V1 and V2 in resin line, V7 and V12 in water line, and V13 and V15 in catalyst line.

8. Switch on flow controllers making sure that their settings are at zero.

9. Open valve V10 and activate pump P4 to transfer contents of liquid waste drum into tank TK2. After an appropriate time to permit emptying the drum, close V10 while opening V9 simultaneously thus allowing the waste in tank to be well mixed. Withdraw a solution sample via valve V11 and determine its pH. Add appropriate amounts of acid/base (gravity feed) to adjust tank solution pH to desired level. Additional sampling would be required to ascertain final pH. Finally, switch off pump P4 and close valve V9.

Operation Phase

1. Switch on emulsifying head (light on panel turns green) and line blender.

2. Initiate resin flow by gradually increasing setting on resin flow controller to obtain the desired flow rate (based on resin flow calibration).

3. Start waste flow by gradually increasing setting on waste flow controller to obtain the desired flow rate (based on waste flow calibration).

4. Ensure a satisfactory emulsion is being produced and then initiate catalyst flow by gradually increasing setting on catalyst flow controller to obtain the desired flow rate (based on catalyst flow controller).

5. Collect catalyzed emulsion in product container.